

TEMPERATURE PROGRAMMING IN GAS CHROMATOGRAPHY

by

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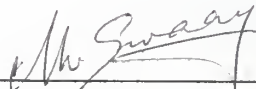
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## CHROMATOGRAPHIC THEORY

Gas chromatography is a versatile, relatively new analytical technique. Chromatography's history dates back to the work of F. F. Runge in 1850 (1). The usefulness of gas chromatography became apparent in the decade beginning in 1950. Since then researchers have found gas chromatography useful in a wide range of separation and identification problems involving both organic and inorganic problems.

Gas-liquid chromatography is a process based on partition equilibrium of a vapor between a stationary liquid phase dispersed on a porous solid support and a moving gas phase. Volatile mixtures can be separated into components when each component has a different distribution coefficient between the liquid phase and gas phase.

The time between injection of a compound into the column and its elution and detection is  $t_R$ , the experimental retention time. This retention time is directly proportional to the volume of gas that is needed to elute the compound. This volume is referred to as  $V_R$ , the experimental retention volume. These parameters are related by

$$t_R v = V_R \quad (1)$$

where  $v$  is the carrier gas flow rate measured at the end of the column.

The ratio of the amount of solute in the liquid phase to that in the gas phase is denoted by  $k$ , commonly called the capacity ratio. In gas-liquid chromatography, the retention volume, the partition ratio, and the retention volume of some nonsorbed gas  $V_a$ , are related by

$$V_R = V_a (1+k). \quad (2)$$

We may eliminate the dead volume,  $V_a$ , of the column

which is a constant contribution to retention volume by defining a net retention volume  $V'_R$ :

$$V'_R = V_R - V_a = kV_a. \quad (3)$$

Similarly we may define the net retention time,  $t'_R$ :

$$t'_R = t_R - t_a = kt_a. \quad (4)$$

in which  $t_a$  is the time required for elution of a nonsorbed compound.

The flow rate of the carrier gas measured at the end of the column can be related to the velocity of the carrier gas through the column. However, the linear velocity is not constant; it varies as a function of position along the column. This variation is a function of the pressure drop which can be measured at points along the column. The pressure at position  $x$  is related to the inlet and outlet pressure by

$$\frac{x}{L} = \frac{(p_i/p_o)^2 - (p_x/p_o)^2}{(p_i/p_o)^2 - 1} \quad (5)$$

where  $L$  is the length of the column,  $p_i$  and  $p_o$  are inlet and outlet pressures respectively, and  $p_x$  is the pressure at position  $x$ , where  $x$  is the distance measured from the column inlet. The above equation is referred to as the pressure correction factor and was developed by James and Martin.

The linear velocity of gas at position  $x$  may be calculated by substitution of the relation

$$u_o/u_x = p_x/p_o \quad (6)$$

into equation number (5), where  $u_o$  is the velocity at the outlet of the column and  $u_x$  is the velocity at position  $x$ . It is useful to know the average pressure,  $\bar{p}$ :

$$\bar{p} = \frac{\int_0^L p dx}{\int_0^L dx} \quad (7)$$

This integration gives

$$\bar{p} = \frac{2}{3} P_0 \frac{(P_1/P_0)^3 - 1}{(P_1/P_0)^2 - 1} \quad (8)$$

The average velocity  $\bar{u}$  along the column may be expressed as (2):

$$\bar{u} = \frac{u_0 P_0}{\bar{p}} \quad (9)$$

The capacity ratio is related to the partition coefficient,  $K$ , by

$$k = K V_1 / V_g \quad (10)$$

where  $K$  is the concentration in the liquid phase divided by the concentration in the gas phase. The letters  $V_1$  and  $V_g$  represent the volumes of liquid and gas phases contained in unit length of the column. The partition coefficient,  $K$ , is a thermodynamic parameter which can be used to identify a sample component, if the partition coefficient is directly proportional to the net retention time,  $t'_R$ . This can be shown by solving equation (4) for the partition coefficient and expressing  $t_a$  as  $L/\bar{u}$ :

$$t'_R = L/\bar{u} [K(V_1/V_g)] \quad (11)$$

The partition of a component in the column between the liquid phase on the inert support and the mobile gas phase may be treated as a chemical equilibrium. The equilibrium constant is the partition coefficient; which is the ratio of the concentration of solute in the liquid phase to the



concentration of solute in the gas phase. The partition coefficient is a function of temperature and of the molar free energy charge,  $\Delta F$ . Thus the distribution coefficient,  $K$ , can also be related to the molar heat of solution and molar entropy:

$$\ln K = \Delta F/RT = -\Delta H/RT + \Delta S/R \quad (12)$$

where  $T$  is absolute temperature, and  $R$  is the molar gas constant,  $\Delta H$  is the molar heat of solution and  $\Delta S$  is the molar entropy. From equation (12) it is clear that  $K$ , and any retention parameter based on  $K$ , depend strongly on the temperature. It can be observed from equation (12) that an increase in temperature will decrease the value of the distribution coefficient and thus decrease the retention time.

Operation at high column temperature will shorten analysis time, but this is achieved at the expense of resolution for low-boiling components. When the column temperature is raised during a run, low-boiling components can be eluted with adequate resolution at the low initial temperature, and heavy components can still be eluted in reasonable time at the elevated temperatures reached toward the end of the run.

In addition to  $K$ , other parameters such as mass flow rate and average velocity are affected during temperature-time programs. The change in temperature affects the viscosity of the carrier gas, which in turn affects the average velocity of the carrier. At constant inlet and outlet pressures the velocity profile of the column remains constant; that is, at any point on the column the ratio of the average velocity to local velocity is independent of  $T$ . Therefore, only the average velocity need be known as a function of temperature.

The viscosity-temperature relation was expressed by Golay (3) as:

$$\eta_0/\eta_T = (T_0/T)^\gamma \quad (13)$$

where  $\eta_0$  is the viscosity at starting temperature  $T_0$  temperature in degrees Kelvin, and  $\eta_T$  is the viscosity at absolute temperature  $T$ . For helium  $\gamma = 0.7$ . At constant flow at the outlet of the column, the average velocity depends upon temperature, and its variation can be predicted from the gas laws.

At constant inlet and outlet pressures the pressure profile along the column is independent of temperature only if the column is uniformly heated.

The gas flow in a column under constant inlet and outlet pressure is not a constant during a programmed-temperature run. Therefore, a detector which is insensitive to gas flow is required. Hydrogen flame ionization detectors are useful for such systems, because they are largely insensitive to flow rate.

Although the distribution coefficient can be calculated from retention data, this requires knowledge of the value of a number of experimental parameters, some of which are not easily accessible. The difficulties may be eliminated in isothermal chromatography by the use of relative retention data, whereby the retention is expressed relative to the retention of one or more of a series of reference compounds. This concept has been developed by Kovats (4).

In programmed temperature gas chromatography, retention data may also be used for identification purposes, but the situation is complicated because the retention of a given compound depends on the time-temperature

program of the column during the analysis. Excellent theoretical work has been done on the calculation and interpretation of retention data in programmed temperature analysis, notably by Golay (5) and Giddings (6), but practical applications are hampered by uncertainty about actual column temperatures.

A retention index for programmed temperature chromatography which is based upon elution temperature of the compound has been proposed by Guiochon (7). The numerical value of Guiochon's index is approximately equal to the Kovats retention index.

Programmed temperature retention data can have a large error due to the lack of reproducibility in the temperature program(8). Habgood and Harris greatly increased the usefulness of the retention indices,  $I_{Pr}(x)$ , in programmed temperature gas chromatography by showing that retention indices can be calculated from isothermal data (9). Thus the retention time or temperature in temperature programmed gas chromatography can be predicted from isothermal data.

The usefulness of programmed temperature gas chromatography could be significantly increased if reproducible and accurate linear temperature programs could be developed. The retention indices for compounds eluted from a column with a known linear temperature program would be as useful as isothermal retention indices. To date, there are no commercially available chromatographs which have temperature programs which are both accurate and precise to the degree needed for useful programmed temperature retention indices.

## DESIGN OF THERMOSTAT:

### I. Theory

Presently available commercial equipment depends upon heat transfer from a thermostat to the column by air convection or direct conduction. In such systems there is an inherent time lag between the air temperature and the column temperature. This leads to an uncertainty in the column temperature, the magnitude of which depends on the time lag. Time lag  $\tau$  can be calculated from

$$C/G_{\text{eff}} = \tau \quad (14)$$

where  $G$  is heat transfer coefficient and  $C$  is column heat capacity. The time lag can be related to temperature lag,  $\Delta\lambda$ , between temperature of the thermostat and the actual temperature of the column by

$$\Delta\lambda = (dT/dt)\tau \quad (15)$$

in which  $dT/dt$  is the rate of heating of the thermostat. The minimum  $\tau$  for commercial equipment is about 15 seconds. It may be as large as 100 seconds or more, but then the equipment is seldom claimed as suitable for programmed temperature gas chromatography. Thus the magnitude of the temperature difference depends upon the heating rate; for a normal program rate, the temperature difference can be as much as  $15^{\circ}\text{C}$  and is seldom less than  $1^{\circ}\text{C}$ . This temperature discrepancy in turn will affect the reproducibility of the program and thus the reproducibility of the retention data.

The time-temperature discrepancies can be corrected by placing a thermocouple on the column and measuring the time-temperature program for each run. This would increase the usefulness of programmed

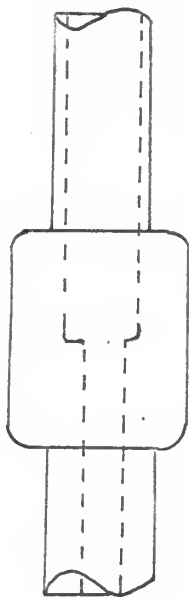
temperature retention indices, but also complicate a now simple analytical method. The programmed runs would be simple and provide useful retention data if the column time-temperature relation were accurately known and reproducible. A thermostat has been developed which has temperature control to  $0.2^{\circ}\text{C}$  during a repeatable program run. This is achieved by ohmic heating of an adiabatically mounted column.

The purpose of this thermostat is to achieve a temperature program of a gas chromatographic column which can be accurately predicted from constants obtained from the column. Heat is generated in the column by means of an electrical current. The temperature of the surrounding air bath is kept at the same temperature as the column. Thus there is no heat transfer to or from the column. In the absence of heat loss the temperature of the column is determined from the electrical energy input and the heat capacity of the column. Stray heat transferred,  $\Lambda$ , to the column depends on two factors: the heat transfer coefficient  $G_i$  between the column and its surroundings, and the temperature gradient  $\Delta T$  between the column and its surroundings; i.e.,

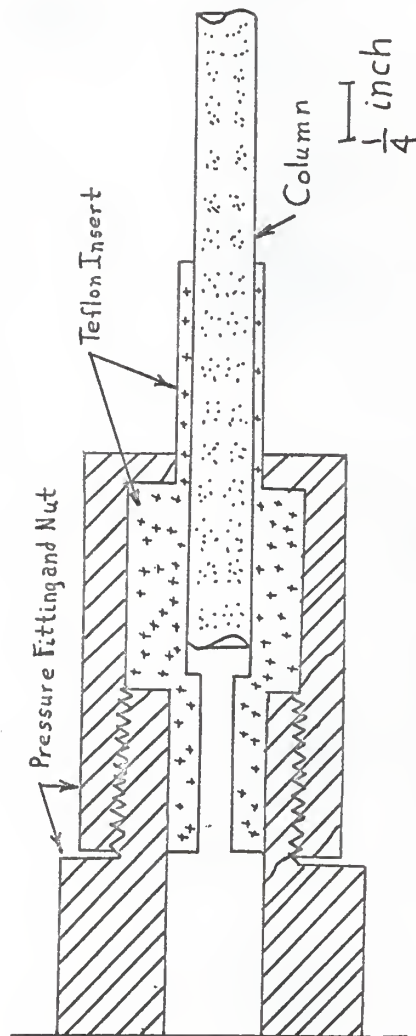
$$\Lambda = \Delta T G_i \quad (16)$$

where  $\Lambda$  is the heat leak from the thermostat. For proper operation  $G_i$  and  $\Delta T$  should be small. We can recognize two factors contributing to  $G_i$ : air convection, and conduction through column connectors and temperature sensors. Column connectors are thermally and electrically insulated by small Teflon inserts (Fig. 1); thin wire thermocouples. (#36 copper-constantan) are used as temperature sensors. The thermal gradient  $\Delta T$  across all heat leaks is kept small by control of the temperature of the air bath surrounding the column container and by

FIGURE 1  
Teflon Insert



## Teflon Insert



Teflon Insert shown with Column and Half of a  
Pressure Fitting

providing good thermal contact between the air bath and the leads and tubing connected to the column. The result of these measures can be described in terms of an effective heat transfer coefficient  $G_{eff}$  from the column to atmosphere.

The power output,  $P$ , to the heater of the thermostat at constant load is directly proportional to the temperature difference between the column and the thermostat.

$$P = A'(T_c - T_T) + P_0 \quad (17)$$

where  $P$  is the power,  $A'$  is a transfer function indicating the sensitivity of the control system,  $T_c$  is the thermostat temperature and  $P_0$  is the steady input power to the thermostat. The temperature difference between thermostat and the laboratory is proportional to  $P$ , so that we may write:

$$T_T - T_0 = A(T_c - T_T) + \gamma P_0 \quad (18)$$

where  $\gamma$  is a power-to-temperature conversion factor, and  $T_0$  is the laboratory air temperature. If a point temperature  $T_s$  is defined as

$$T_s = T_0 + \gamma P_0, \quad (19)$$

then equation (18) can be written:

$$A = (T_T - T_s) / (T_c - T_T). \quad (20)$$

The heat leak away from the column to the thermostat is proportional to the heat transfer coefficient and the temperature gradient:

$$\Lambda = (T_c - T_T) G_i. \quad (21)$$



As seen by the column, the heat leak may also be written

$$\Lambda = (T_c - T_s)G_{\text{eff}}. \quad (22)$$

Combining equation (21) and (22) and simplifying gives

$$G_i/G_{\text{eff}} = 1 + A. \quad (23)$$

If equation (22) is rearranged and  $T_o + \gamma P_o$  substituted for  $T_s$ , an equation for a line of the form  $Y = ax + b$  is obtained:

$$\Delta T = T_p + \frac{\Lambda}{G_{\text{eff}}} \quad (24)$$

where  $\Delta T$  is the temperature difference between the column and the laboratory, and  $T_p$  is  $\gamma P_o$ .

To obtain a linear time-temperature program, allowance must be made for changes in heat capacity and electrical resistance of the column with temperature. The resistance of the column increases as the temperature increases and the heat capacity decreases as the temperature increases. With constant voltage input to the column the two act in opposite directions.

A differential thermocouple monitors the temperature difference between the thermostat and the column: this thermocouple controls the thermostat heating power in such a way that the temperature difference is minimized at all times. The control loop which regulates the power to the thermostat heaters consists of a Philbrick voltage preamplifier and a Honeywell SCR proportional temperature controller. Details are given on page 21.

A system of protecting the temperature of the column by minimizing temperature effect of the surroundings is a guard system. The temperature



of the column is guarded by the thermostat air bath. The guard system can be illustrated by its electrical analog shown in Fig. 2. The circuit can be characterized by a time constant  $\tau = R_1 C(1+A)$ . When this time constant is large, compared to the time required for one experiment, the system may be treated as if the column were mounted adiabatically. It was found experimentally that the system has a time constant of 200 minutes, or approximately 20 times the duration of an experiment.

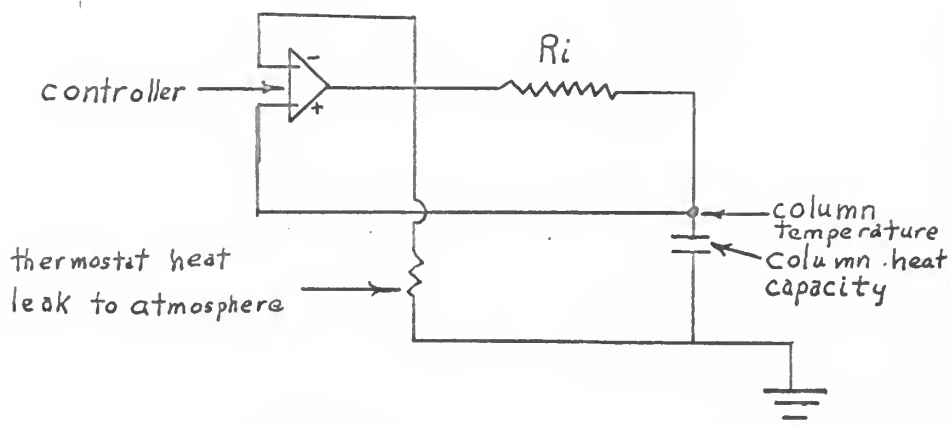
Although the basic circuit of the SCR controller responds to resistance changes, the current through the recommended resistance sensor activates a safety circuit to guard against open and short circuits at the input. It was found that the circuit shown would operate satisfactorily with a minimum of modification of the SCR unit. The variable output current of the Philbrick amplifier through fixed resistance  $R$  is equivalent to a varying resistance in the SCR circuit and safety circuit.

The frequency response of the preamplifier is limited by the 0.3  $\mu$ F capacitor in the feedback path, to attenuate any 60 cycle noise and to eliminate any spurious oscillation of the overall loop. Maximum loop gain was sufficient to drive the SCR output from nought to saturation with a temperature change of approximately  $1.5^\circ\text{C}$ .

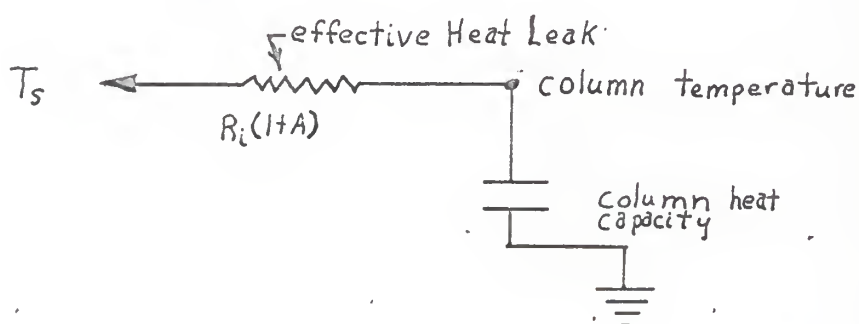
Heating rate of the thermostat at saturation power was found to be greater than  $30^\circ\text{C}$  per minute.

FIGURE 2

## Electrical Analog and Equivalent Circuit of Heat



## Electrical Analog Defining Heat Flow



## Equivalent Circuit Defining Heat Flow as seen by the Column

## DESIGN OF THERMOSTAT:

## II. Construction

In isothermal gas chromatography, the column should have a constant and uniform temperature. In programmed temperature gas chromatography, one should have a known temperature-time profile on the column for a given point on the column and for any time  $t$  all points on the column should be at the same temperature. The thermostat was designed so that the column would have the desired temperature behavior.

Heat is generated directly in the column by means of electrical current, and the air bath around the column is maintained at the same temperature as the column by means of an auxiliary heater. Figure 3 is a schematic diagram of the thermostat. Air is circulated downward around column container 5 through space 1 and upward through annular space 2, containing the heater coils 3. The gas chromatographic column 4 is mounted inside column container 5 which is suspended by means of thin aluminum lead-in tubes 6. The lead-in tubes serve both as containers for all electrical wiring connected to the column and as support for the column container. The temperature of the thermostat is controlled by a Honeywell proportional temperature controller, Model R7187A. The controller is driven by the output of a differential thermocouple (8) monitoring the difference in the temperature between the column and the air bath in the thermostat. The signal from the thermocouple is amplified by a Philbrick SP656 amplifier.

The injection port and heater are the same as used in an Aerograph (10) gas chromatograph; they are mounted on the lid of the thermostat. The injection port temperature control is a variable transformer; thus

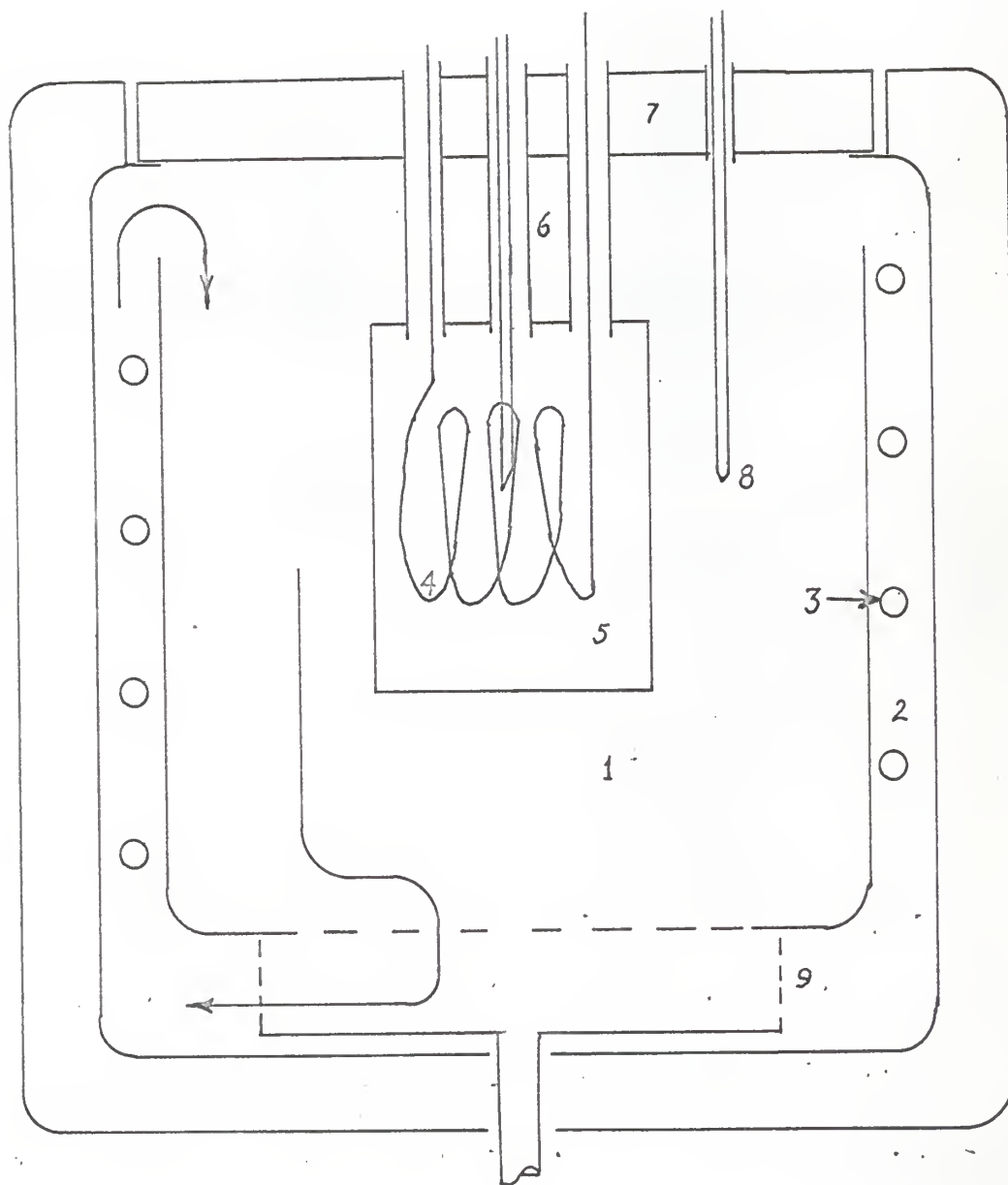
TABLE 1

## Components of Figure 3

1. Air circulation space
2. Air circulation space
3. Heaters
4. Gas chromatographic column
5. Column container
6. Lead-in tubes
7. Lid with insulation
8. Thermocouples
9. Squirrel cage

FIGURE 3

Cut Away Thermostat



it will hold constant temperature only at constant heat loss. The ideal injection port would hold any temperature desired and not lose any heat to the column. However, the injection port is thermally isolated from the column by mounting it on the top of the thermostat. The connecting tube between the column and the injection port passes through the air bath where any needed cooling or heating occurs. The moving phase, nitrogen, is preheated in the air bath before it goes to the injection port.

The chromatographic instrument has several components as shown in Fig. 4. The electrometer of the Aerograph 60 A and its hydrogen ionization detector are the detector and amplifier for the system. The thermostat has been described. The read-out system is a Texas Instruments recorder (11). The potentiometer used to measure temperatures is made by Rubicon and has a resolution of 0.001 millivolt. The readings were made to the nearest 0.001 millivolt.

Figure 5 shows the gas flow diagram for the chromatography set up. The details for the control loop are shown in Fig. 6.

TABLE 2

## Components of Figure 4

- A. Variable transformer
- B. Electrometer, (Aerograph 60 A)
- C. Step down transformer, 100 amp, 10 volt output
- D. Out put recorder (Texas Instruments Servo Recorder)
- E. Line voltage 120 VAC
- F. Igniter
- G. Signal cable
- H. Thermostat
- I. Thermocouple wires (temperature indicating)
- J. Cold junction 0°C
- K. Potentiometer
- L. Differential thermocouple wires
- M. Power line to thermostat heaters
- O. Preamplifier
- P. Honeywell controller

FIGURE 4

Equipment Diagram

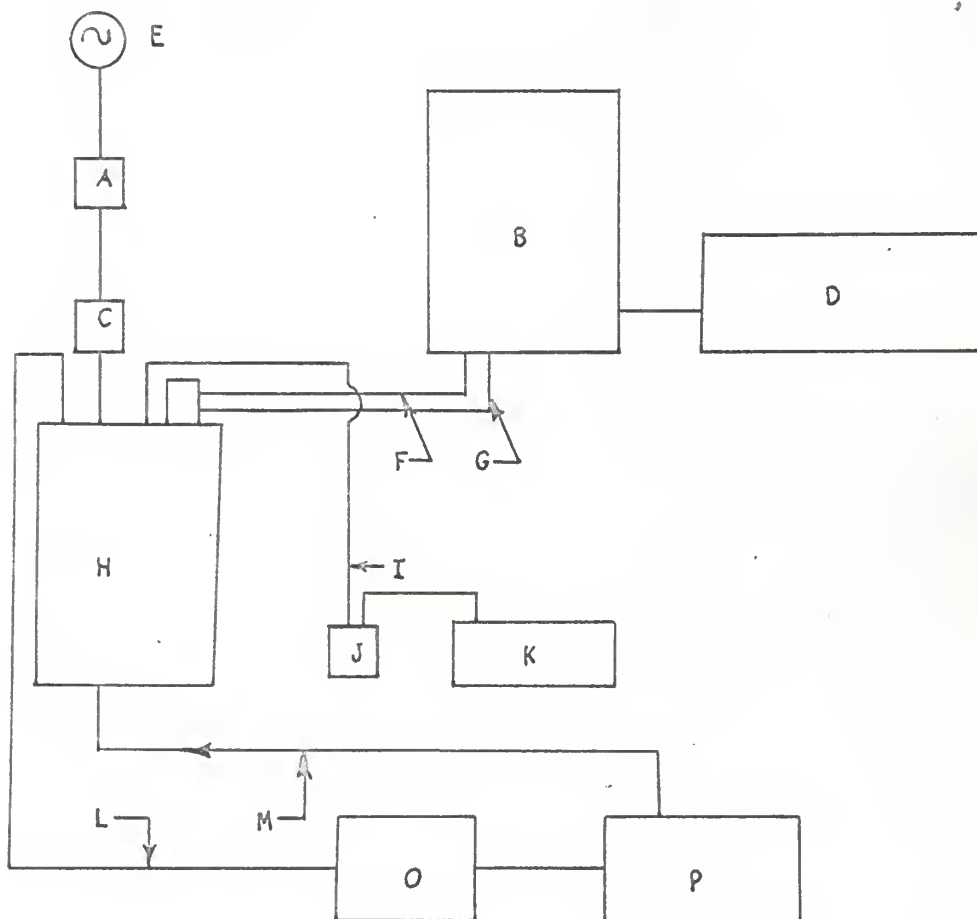




FIGURE 5

Diagram of Instrument Gas Flow

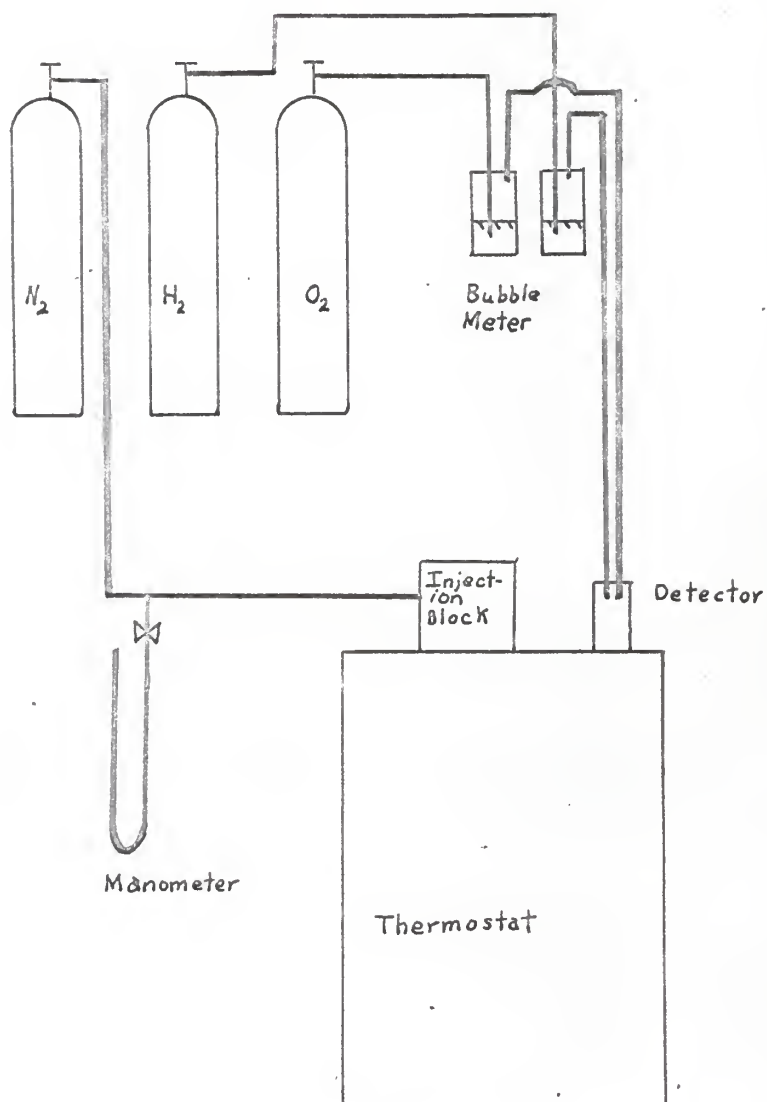
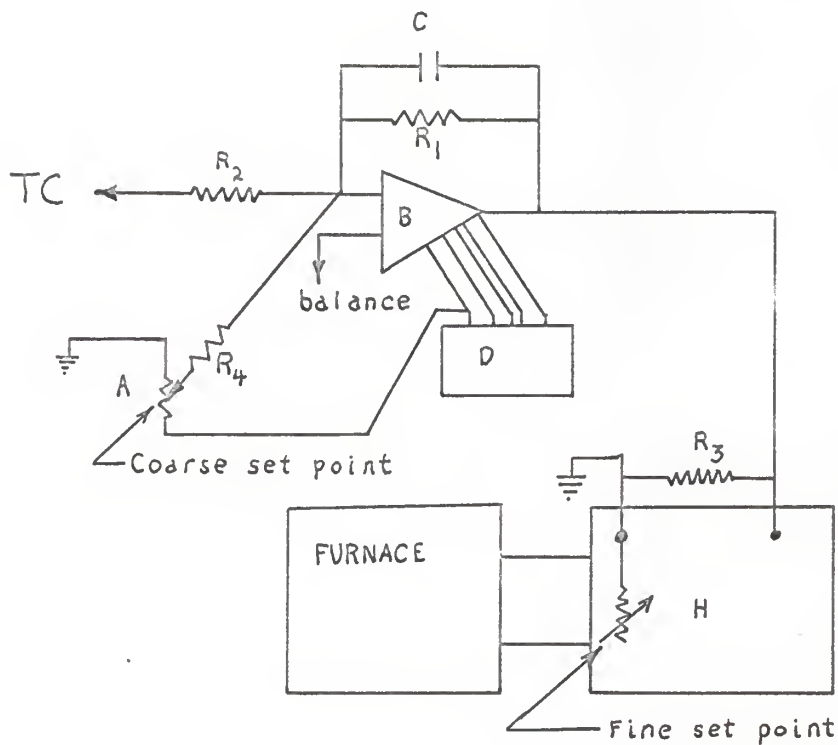


FIGURE 6

## Philbrick Amplifier and Honeywell Controller

## Wiring Diagram



- A. Coarse set point with reference
- B. Philbrick amplifier # SP656
- C. Capacitor, 0.3 $\mu$ F
- D. Power supply,  $\pm 15$  VDC, 6.3 VAC
- H. Honeywell proportional temperature controller R7187A
- R<sub>1</sub> 1M ohm
- R<sub>2</sub> 100 ohm
- R<sub>3</sub> 1000 ohm
- R<sub>4</sub> 1M ohm

## OPERATION OF THE PROGRAMMED TEMPERATURE GAS CHROMATOGRAPH

For satisfactory operation of the programmed gas chromatograph, the starting conditions should be reproducible. The injector port should be hot enough to quickly vaporize the highest boiling fraction. The injection port must be at the same temperature at the start of each run. The temperature of the column must also be at the same starting temperature if identical runs are desired. If the starting temperature is higher, the peaks will elute earlier but at a predictable temperature. The starting conditions for the experiments were kept constant by allowing the column to cool to a constant temperature. This temperature was reproducible between runs. The injection port loses the heat gained during the previous run and its temperature is easily reproduced by allowing conditions to come to an equilibrium. The amount of heat the injection port gains during a run does not affect the temperature of the column, because there is no heat transferred to the column from the injection port. If the injection port is below the boiling point of any of the components injected, the heat gained by the injection port affects the rate of evaporation of high boiling fractions and thus their retention time. It was found that the temperature of the port at the end of the run was reproducible if the starting conditions were the same.

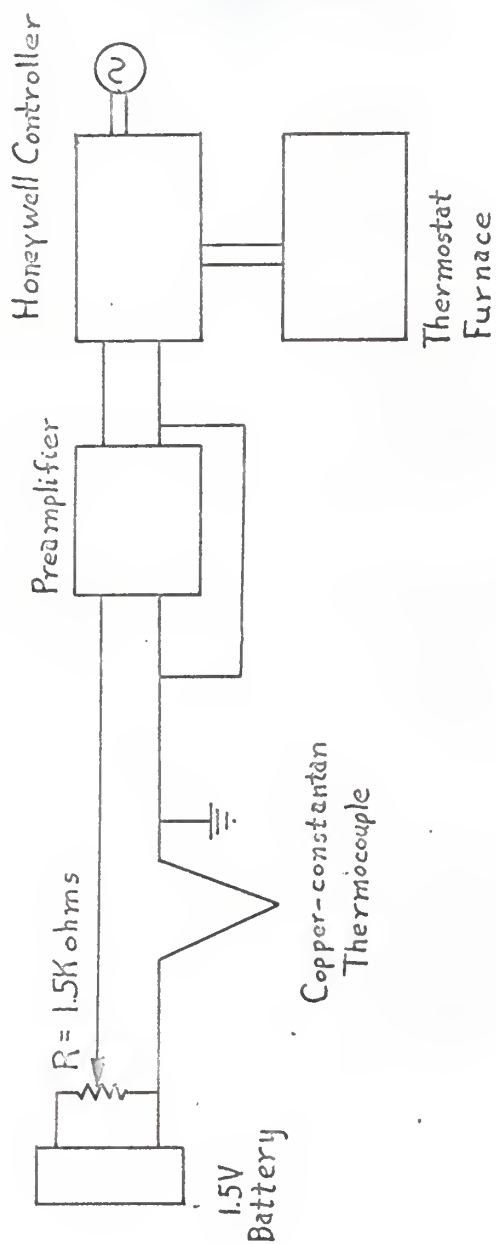
For each run gas inlet pressure was adjusted so that  $p_i/p_o$  was 1.77. The starting temperature of both the column and the injection port was checked and adjusted if needed. The recorder was started and when the pen crossed a marker, the sample was injected and a stop watch was started. The Honeywell temperature set and its proportional band should

be pre-set at optimum conditions. When ten seconds have elapsed, power is supplied to the gas chromatographic column. (See Fig. 18 for a typical heating curve.)

The procedure followed for constant temperature chromatography was the same as that for programmed gas-liquid chromatography except that ohmic heating of the column was omitted. To obtain a constant temperature the column thermocouple was replaced by a reference signal from a battery and voltage divider. Thus this constant signal forced the guard ring to keep an air bath of constant temperature around the column. The temperature of the air bath and the column is directly proportional to the signal from the battery and voltage divider. (See Fig. 7 for circuit diagram.)

FIGURE 7

Isothermal Circuit



## PERFORMANCE

The linearity of the heating rate of the column and the predictability of the retention times for compounds is a measure of the performance of the instrument. The heating characteristics of the column and the linearity of heating rate were determined. Retention times and retention temperatures of compounds were predicted from isothermal data and compared to the actual values obtained from programmed gas-liquid chromatography.

### I. Thermal Tests

Direct heating is useful only if the temperature distribution along the column during the heating cycle is uniform. Several experiments were carried out to determine this. The purpose of the experiments was to find a means to sense the temperature on a column during a temperature change and to determine the temperature profile along a typical column.

Several methods of determining the column temperature were tried. Thermocouples were the sensors for all experiments; the method of attachment to the column and the size of the thermocouple wire was varied. It was desirable to have a thermocouple which could quickly respond to a small change in temperature. The material finally chosen was wire, 0.013 centimeter diameter copper and constantan (B & S #36). The time lag for these thermocouples in measuring a change in still air from 800°F to 100°F was 5 seconds.

To test the responses of the thermocouples, various methods of attaching the thermocouples were compared. The wires were attached to three feet of copper tubing which was silver soldered to a brass block which served as a heat sink. The brass block was heated, and heating and

cooling curves of the tube at the points of connection were determined.

In the experiment four thermocouples were placed around the tube equidistant from the heat sink. One thermocouple was soft soldered onto the tube, two were attached with Omega Thermcoat, and one was taped onto the tube with glass tape. The thermocouple that was soft soldered onto the tube had the smallest temperature lag, thus it also had the smallest time lag. (See Fig. 8 for results.) Assuming that all points of attachment were at the same temperature, the most desirable method of attachment is soft soldering. This result is expected because a good electrical conductor such as solder is also a good heat conductor.

Soft soldering a thermocouple onto a column limits the column temperature to the melting point of solder. Another disadvantage of using soldered or brazed junctions is that additional unwanted heat capacity is added to the column.

Attaching the thermocouples to the column by means of a spot weld offered a logical alternative. The heat transfer should be excellent and a minimum of additional heat capacity would be introduced.

An experiment was done to compare the efficiency of the thermocouples attached by a weld to that of a thermocouple attached by lead solder. There were two welded thermocouples, one had the copper wire 1 millimeter from the constantan wire, the other had 3 millimeters difference between the two wires. One millimeter was as close as the wires could be conveniently and reproducibly attached with a spot welder. The third thermocouple was soldered onto the column. The soldered thermocouple was attached first; then the other thermocouples were spot welded in close proximity to the one soldered. The results of the experiment are shown in Fig. 9. The temperatures indicated by each method

FIGURE 8

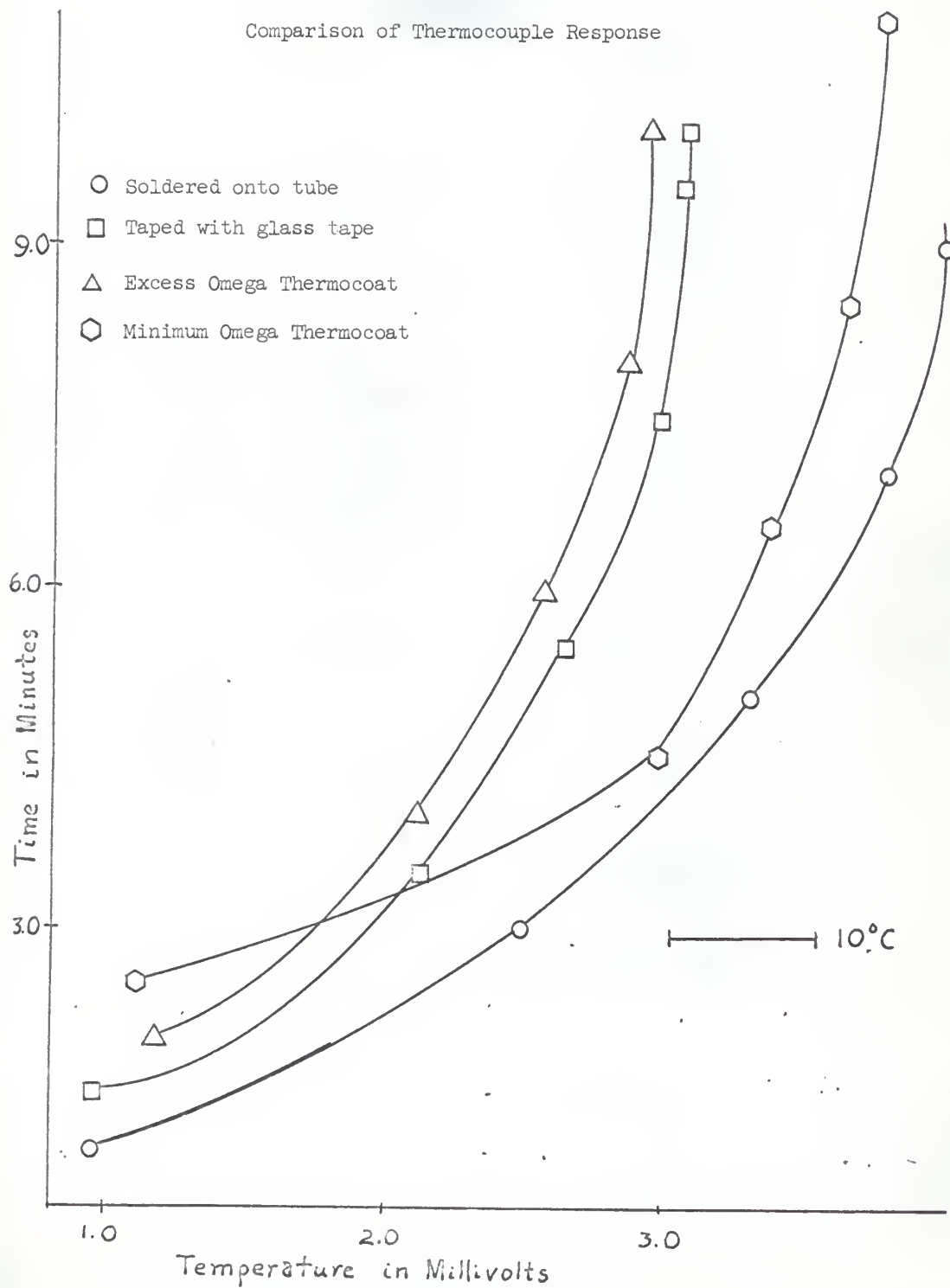
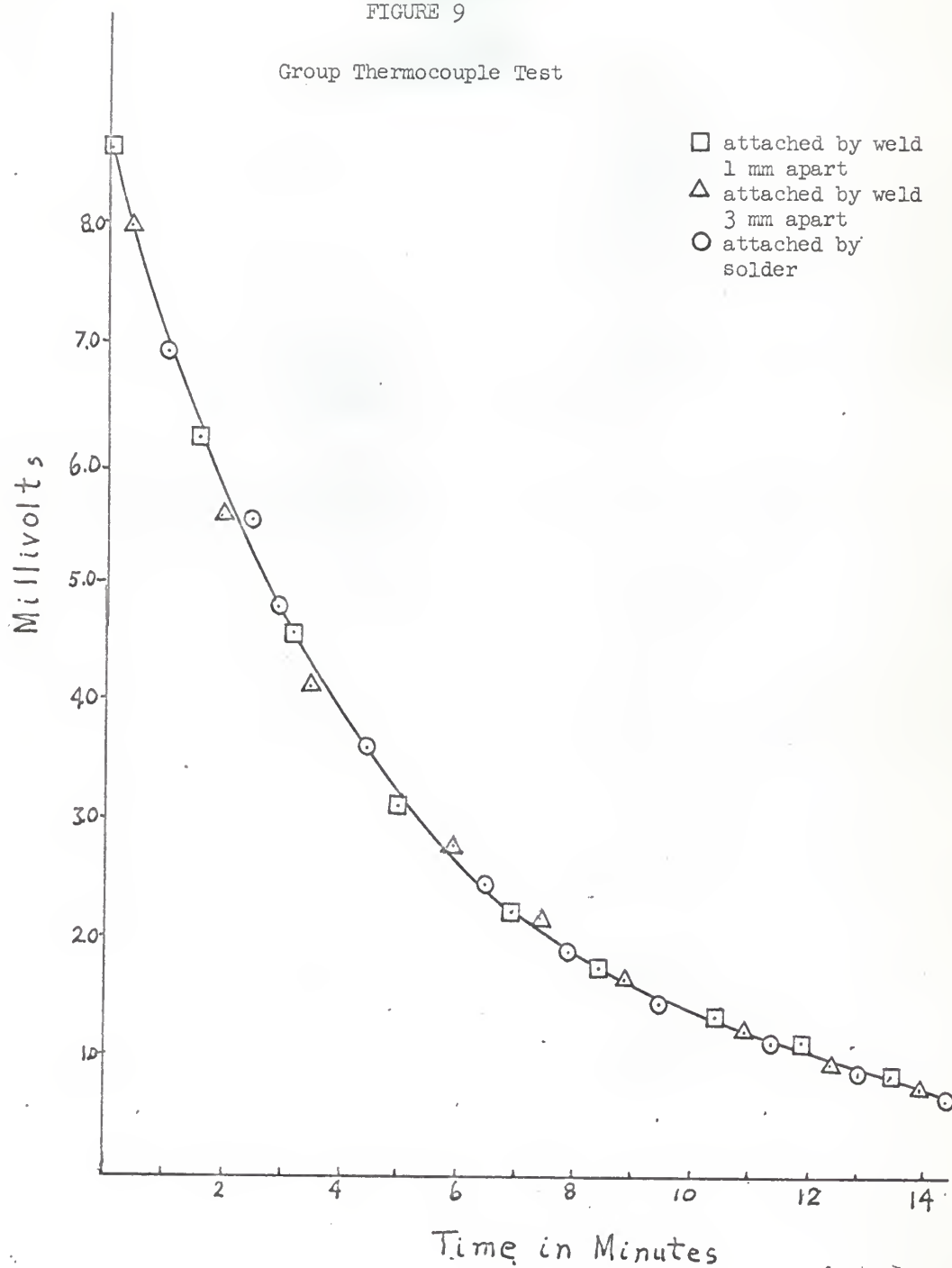




FIGURE 9

Group Thermocouple Test



showed no significant difference graphically. Thus spot welded thermocouples will sense the column temperature, and 3 millimeters difference between the thermocouple ends introduced negligible error.

The temperature along a column must be uniform. One problem for a column which is heated ohmically is the occurrence of hot spots due to local work hardening of the metal which increases the electrical resistance. Work-hardened areas due to bends in the tubing will cause hot spots. An experiment was done to find out if these effects were significant. Two thermocouples were placed on a stainless steel 1/8 inch O.D. tube, one on a straight portion and one on a sharp curve. The tube was wrapped in glass wool and heated ohmically. The results are shown in Fig. 10. The curved part of the tube definitely heated faster than the straight part. The cooling curve (Fig. 11) indicated that both portions of the curve were equally insulated. The apparent discrepancy of the temperature between the two curves is due to the fact that the two points sensed started cooling at the same time, but at different temperatures. Thus we can detect hot spots that result from work-hardening.

The column which was used in the chromatographic experiments was likewise tested for uniformity. The sensors were spot welded on the column and connected to the lead-out wires. The copper side of the 36 gage thermocouple was connected to a 22 gage copper wire. All wires are insulated from one another but not from the column. The potential was measured on a floating potentiometer. The column remained isolated electrically. Temperature profile of the carbowax column was determined during a programmed temperature run,  $10^{\circ}\text{C}/\text{minute}$ . A total of ten thermocouples was placed on the column, particularly at suspected hot

FIGURE 10

Test for Hot Spots Due to Work Hardening:

Heating

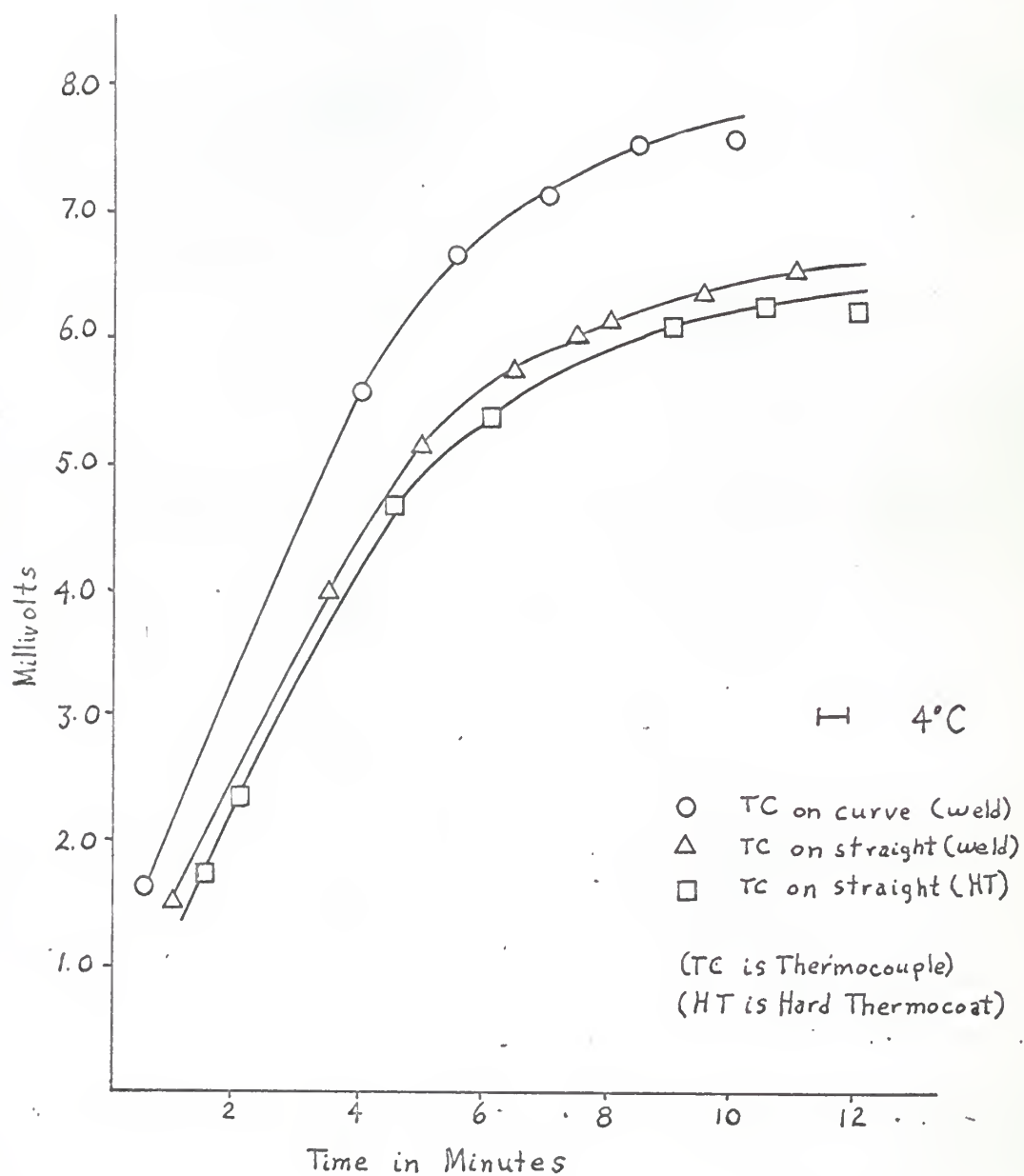
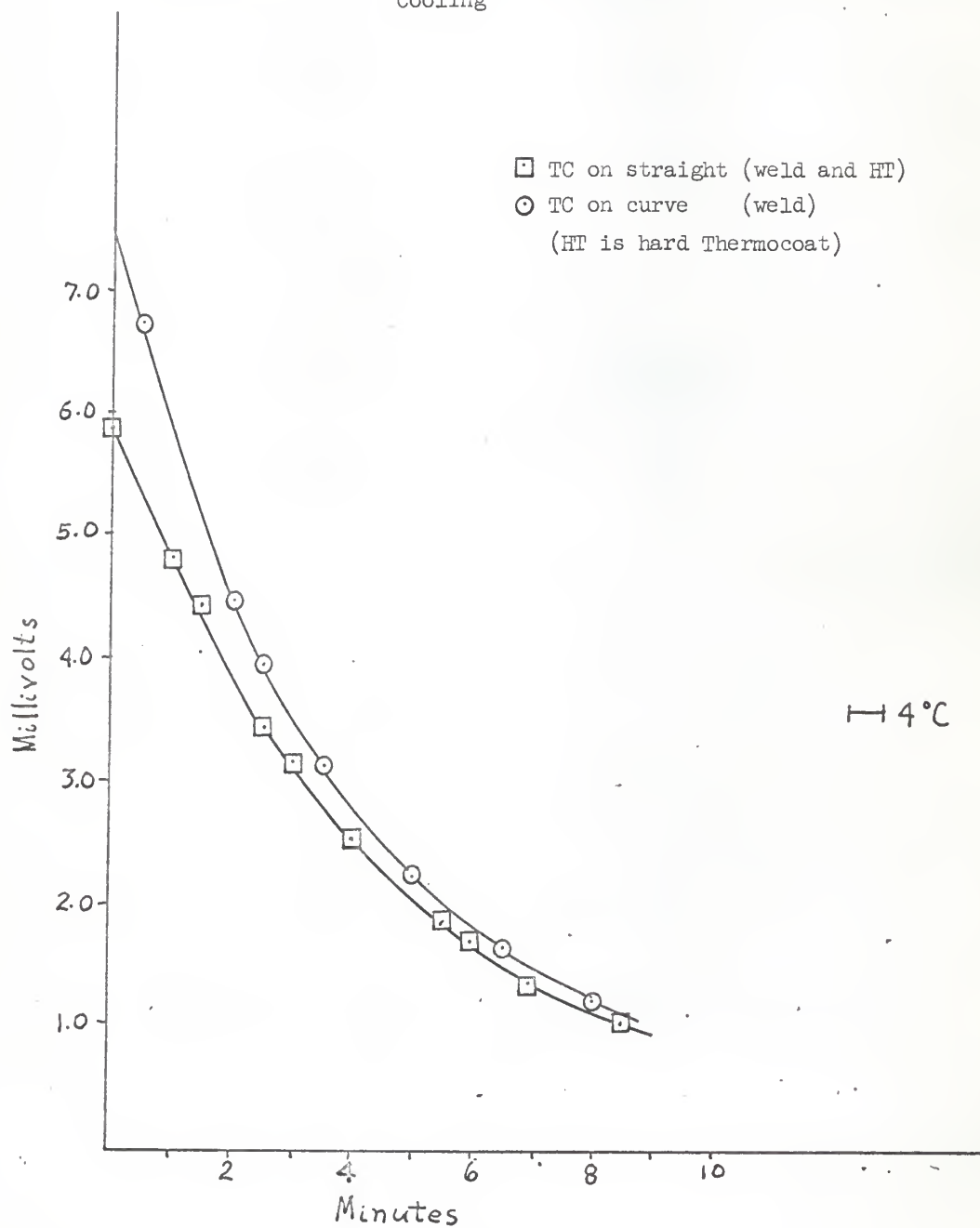


FIGURE 11

Test for Hot Spots Due to Work Hardening:

Cooling



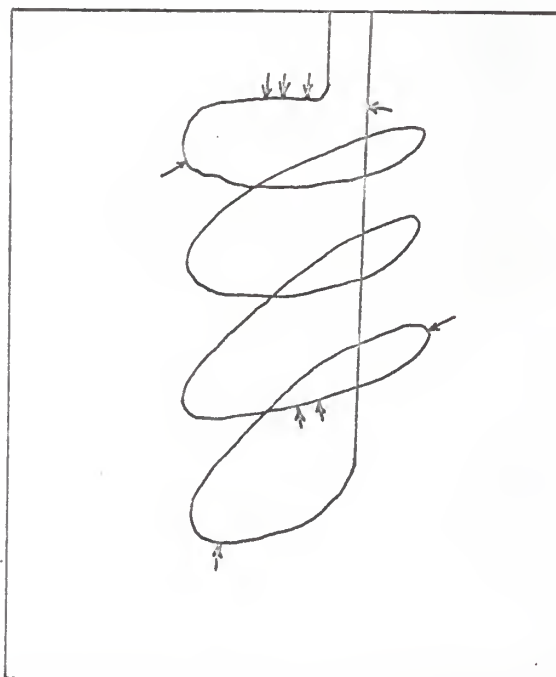
or cold spots. See Fig. 12 for an illustration of the placement of the thermocouples. The results of the experiment are shown in Fig. 13. The time-temperature plot of the run by least squares method indicated that the column had a uniform temperature at any time  $T$ . A simple regression analysis of the data verified the linear relationship of the data. The deviation about the regression was 0.00165 millivolts which is equivalent to  $0.2^{\circ}\text{C}$ . The variance of millivolts was  $0.00002 \text{ mv}^2$  or  $0.0004^{\circ}\text{C}^2$ . The variance of the slope was  $0.00093(\text{mv/min.})^2$  or  $0.018 (^{\circ}\text{C})^2$ . The correlation coefficient was 0.99952. All the thermocouples indicated the same temperature at different points along the curve when the readings were corrected for the heating rate. Thus any end effect is within the limits of error.

The thermostat was developed to have a large heat transfer resistance or a small heat transfer coefficient (explained in the design theory section). The time constant,  $\tau$ , for the thermostat is a measure of how well the column has been insulated by the guard system.

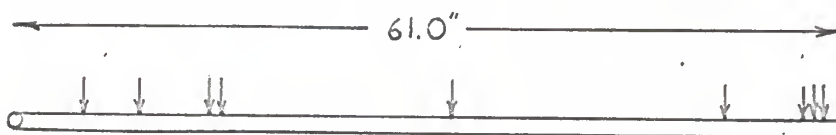
The time constant was determined experimentally. The cooling curve of the column was determined. The Honeywell controller temperature offset and the preamplifier offset were the same as that used for the programmed runs. The column and thermostat were heated to  $167^{\circ}\text{C}$  and then the system was allowed to float. The column slowly cooled (Fig. 14). The time constant,  $\tau$ , was determined to be the time for 67% of the temperature difference to diminish. A time constant of 200 minutes was found for the thermostat.

FIGURE 12

## Placement of Sensing Thermocouples



Column container with column and indication of thermocouple positioning



Position indication for thermocouples on column if straightened

FIGURE 13  
Test for Uniform Column Temperature

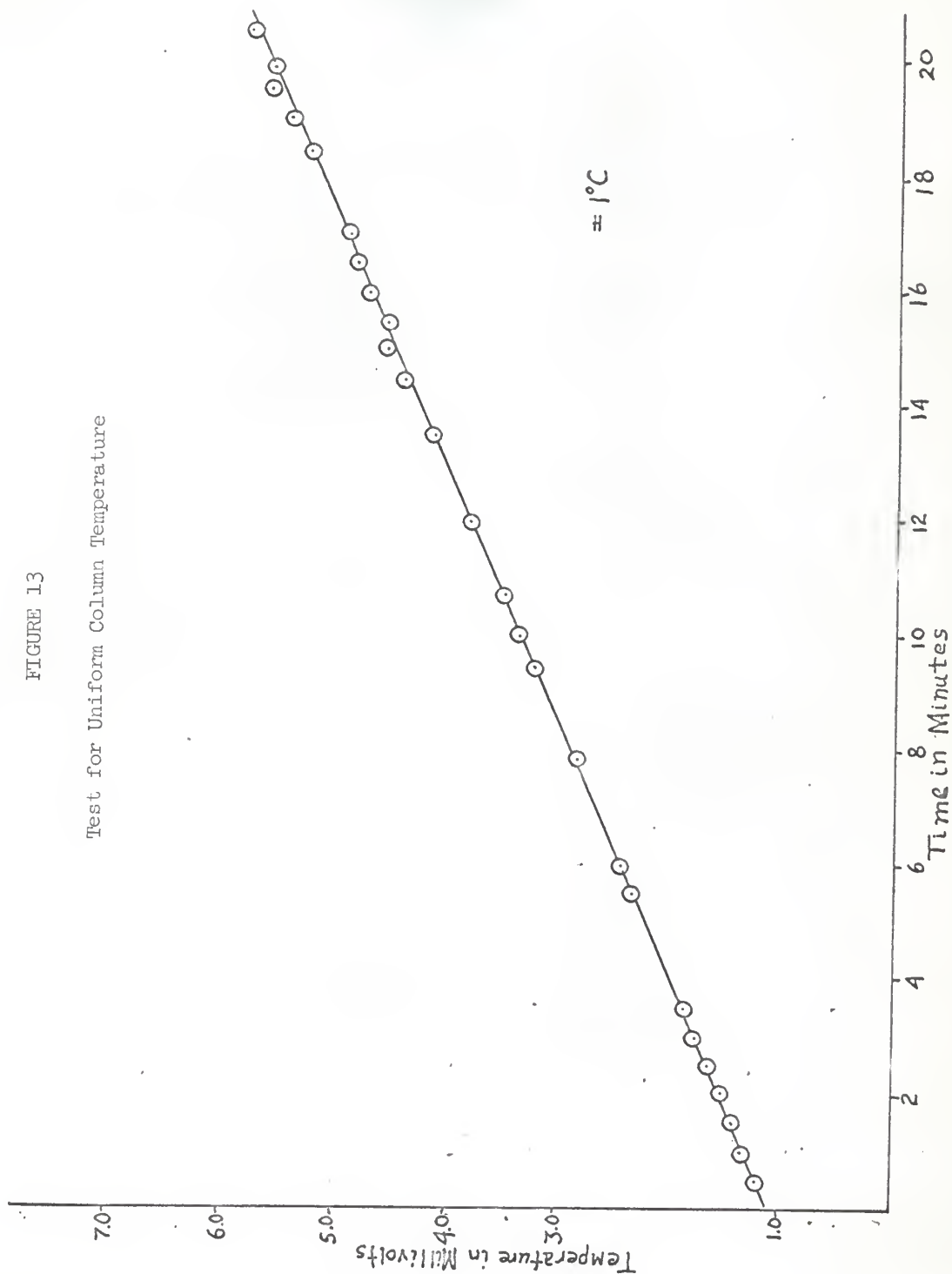
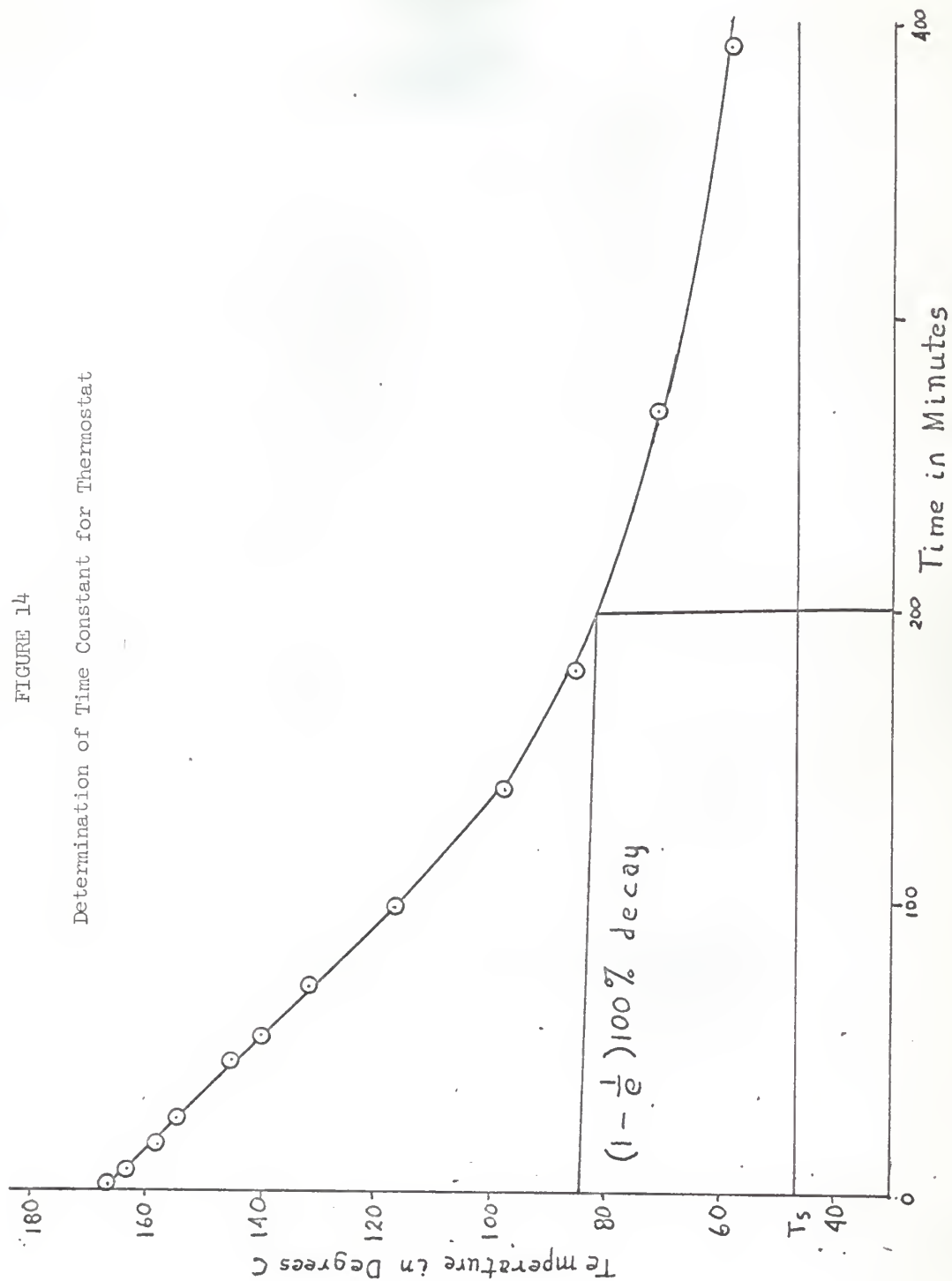


FIGURE 14  
Determination of Time Constant for Thermostat





## II. Programmed Temperature Gas Chromatography Tests

The operation of the thermostat was tested chromatographically by a comparison of the experimentally determined programmed temperature retention data with data predicted from isothermal runs under the assumption of linear heating rate. Correlation of programmed temperature data with isothermal data for known time-temperature profiles has been well established by others (12).

The isothermal chromatography provides data to be used for predictions of retention times for the programmed runs. The operating conditions must be compatible to both isothermal and programmed run prerequisites. The isothermal data should be accurately known and reproducible so that the data introduce a minimum error into the predictions of the retention times for programmed runs.

Isothermal chromatography operating conditions are constant mass flow rate and constant average velocity. This is achieved by having constant inlet and outlet pressures of the carrier gas. Most detectors function well with these conditions. However, in programmed gas-liquid chromatography the mass flow rate of the carrier gas changes with column temperature. Thus detectors such as the thermal conductivity detectors which are commonly used with programmed chromatography cannot be used unless measures are taken to maintain constant mass flow. Constant mass flow is achieved by varying the inlet and outlet pressures, but then the average gas velocity and pressure drop are complicated functions of temperature. Because it is impossible to have constant volume flow in the column, the most convenient operation is at constant inlet and outlet

pressures. Under these conditions the velocity profile along the column is constant, and only the average velocity changes with temperature. A detector insensitive to mass flow, the hydrogen flame ion detector, was used to simplify the technique.

For isothermal work the control circuit was altered to function with a voltage divider and battery. (See Fig. 7 for the circuit details.) No thermal drift could be detected during isothermal runs with the equipment used.

The retention time,  $t_R$ , depends upon the compound, inlet and outlet pressures, temperature of the column, the partition coefficient, the amount of liquid and gas phase contained per unit of the column and the length of the column. (Refer to theory section and equation number 11.) Operation at constant inlet and outlet pressure gives the simplest mathematical equations for treating the average carrier gas velocity, a constant for isothermal work and a function of temperature only for programmed gas-liquid chromatography. In both isothermal and temperature programmed gas chromatography, the partition coefficient will be the same at a given temperature,  $T$ , which is known as a function of time. In isothermal chromatography the velocity at position  $x$  depends only on the inlet and outlet pressures, but in programmed temperature gas chromatography the velocity also depends on the temperature. The other parameters which affect the retention time are the physical characteristics of the column; these do not change with time or temperature and are constant for all runs.

The isothermal retention time,  $t_R$ , at a specific temperature can be related to peak velocity in linearly programmed temperature experiments

at that same temperature if the time and temperature can be accurately related. The retention times for a series of compounds at 20 temperatures were obtained.

The mixture used for these experiments consisted of eight linear hydrocarbons: n-hexane, n-heptane, n-octane, n-nonane, n-decane, and n-dodecane. The percent composition varied so that hexane was least and dodecane was most. Samples of 0.5  $\mu$ l were used for all runs; they were injected with a 10  $\mu$ l Hamilton syringe. Time was noted on the strip chart every three minutes during the first 10 minutes and then every 15 minutes for the rest of the experiment. When it was convenient, the time of peaks maxima were noted on the strip chart. A typical isothermal chromatogram is shown in Fig. 15.

The isothermal runs were made at approximately 10°C intervals between 62°C and 200°C. The retention times of the components were calculated from the distance on the strip chart between injection and elution and detection of the compounds. This distance is directly related to time, the exact relation depending upon chart speed. The distances were measured to the nearest 0.08 centimeter, or 0.12 seconds. The isothermal data are enumerated in Table 3.

The agreement between the retention time calculated from the chart and the retention time noted on peaks was within 1% for all noted compounds with a retention time over 12 seconds. An analytical relation between net retention time  $t'$  and temperature was not found. Golay (12) related the retention time to temperature by:

$$t_R = (T_0/T)^Y e^{-A/(T-T_0)R} \quad (25)$$

FIGURE 15

Typical Isothermal Chromatogram

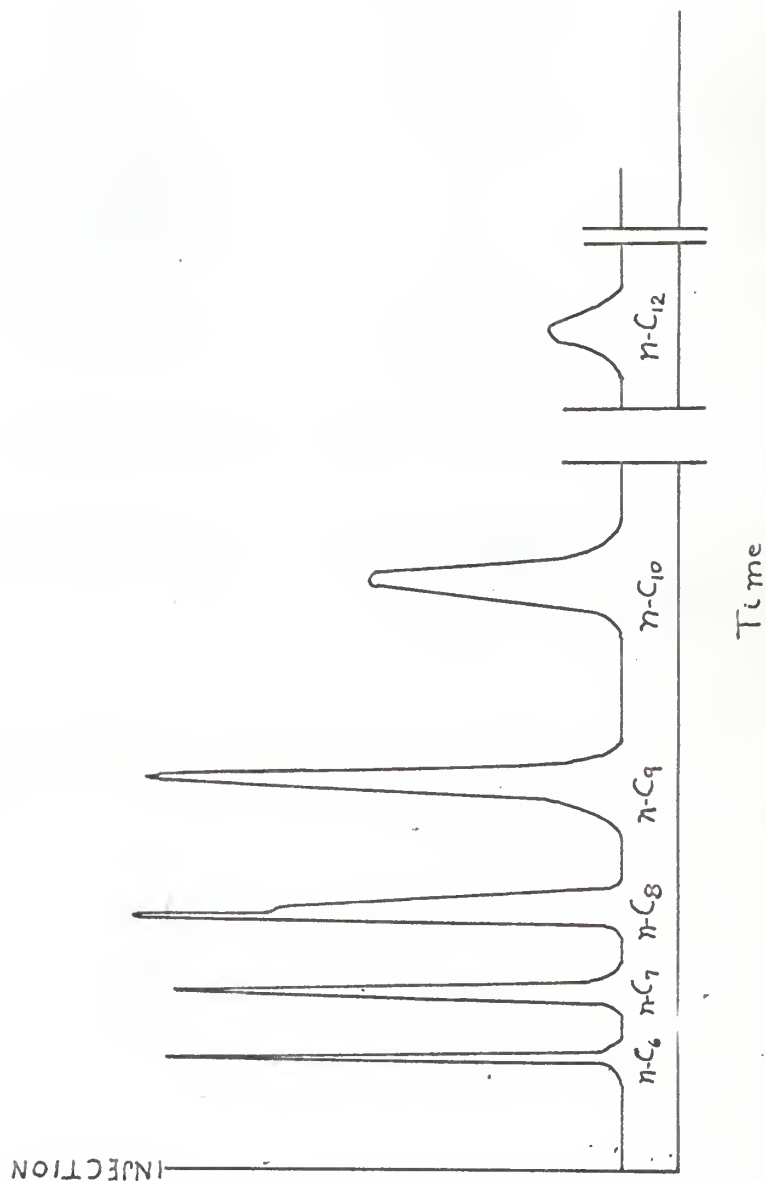


TABLE 3

## Compilation of Retention Data

Temp °A	Net Retention Time in seconds							
	n-c <sub>6</sub>	n-c <sub>1</sub>	n-c <sub>8</sub>	n-c <sub>9</sub>	n-c <sub>10</sub>	n-c <sub>12</sub>	n-c <sub>13</sub>	n-c <sub>14</sub>
354.8	9.6	20.2	41.5	80.9	179.4	590.0	1089.3	2069.0
361.7	9.0	18.3	35.7	65.9	145.0	433.0	817.4	1506.5
369.4	7.1	17.2	32.7	32.7	125.6	355.2	640.8	1161.2
374.3	9.6	16.5	29.0	51.5	111.9	286.5	461.0	854.7
381.4	9.6	15.9	27.1	44.6	97.5	299.0	399.0	699.0
390.5	9.6	15.0	24.2	40.1	87.5	187.7	319.0	699.0
396.2	8.0	13.3	20.0	34.0	78.1	155.2	255.5	424.3
405.0	7.0	10.0	14.0	21.0	53.2	78.3	122.1	191.8
406.9	7.0	11.2	18.7	28.7	64.4	139.0	187.7	303.1
413.5	6.2	9.0	14.6	24.6	58.1	92.1	143.7	228.7
424.6	7.0	9.0	14.0	20.8	53.1	76.5	119.0	182.7
433.0	6.5	9.6	13.3	19.6	49.4	63.1	96.2	145.8
433.0	6.5	9.0	14.0	18.7	50.3	84.7	96.5	145.8
443.9	6.5	9.6	12.1	18.0	45.6	51.2	75.5	110.5
455.7	6.5	6.5	12.4	17.1	43.5	45.0	64.6	92.1
463.1	---	---	---	---	43.7	40.8	54.6	77.1
477.0	---	---	---	---	40.0	32.1	43.3	57.7
477.0	---	---	---	---	40.0	---	44.0	59.0
335.2	---	25.8	74.6	159	349.4	1424.0	2928.7	---
346.0	9.6	24.6	92.7	108	233.8	850.2	1679.9	3211.7

where  $t_R$  is retention time,  $T_0$  is starting temperature in  $^{\circ}\text{K}$ ,  $T$  is the independent variable in  $^{\circ}\text{K}$ ,  $A$  and  $\gamma$  are constants. The constant  $A$  is the free energy change;  $\gamma$  is a viscosity term and  $R$  is the molar gas constant. Equation (25) did not fit the curve within 1% error. To relate net retention time,  $T'_r$ , and temperature, a graph was made. A typical example is Fig. 16. The net retention time was related to temperature by the curve. The graph was used to obtain the net retention time at intervals of  $1^{\circ}$  from  $335^{\circ}\text{K}$ . These data were used to predict the retention time of the compound at a specific linear time-temperature program.

The programmed temperature conditions have already been stated; they were selected to be compatible with the isothermal runs. The method of injection was the same as that used in isothermal work, except that the power to the column was switched on 10 seconds after injection. The chart speed was 1.5 inches per minute throughout the experiment. The distances between injection and detection were related to retention time. A typical programmed temperature chromatogram is shown in Fig. 17.

The temperature of the column during the program was measured as a function of time. From the data the heating rate of column was proven to be linear by linear regression analysis. A typical heating curve is shown in Fig. 18. For carefully prepared programmed heating rates, the sum about the regression was  $0.177^{\circ}\text{C}$ , the standard deviation of the intercept was  $0.2^{\circ}\text{C}/\text{min}$ . The data for the programmed temperature runs will be given later in this section.

The column temperature should rise immediately when ohmic heating is started. The ideal thermostat will have an instant change to the heating rate desired when the program is started. However, the temperature of the

FIGURE 16  
Nonane Isothermal Net Retention Time  
vs.  
Temperature

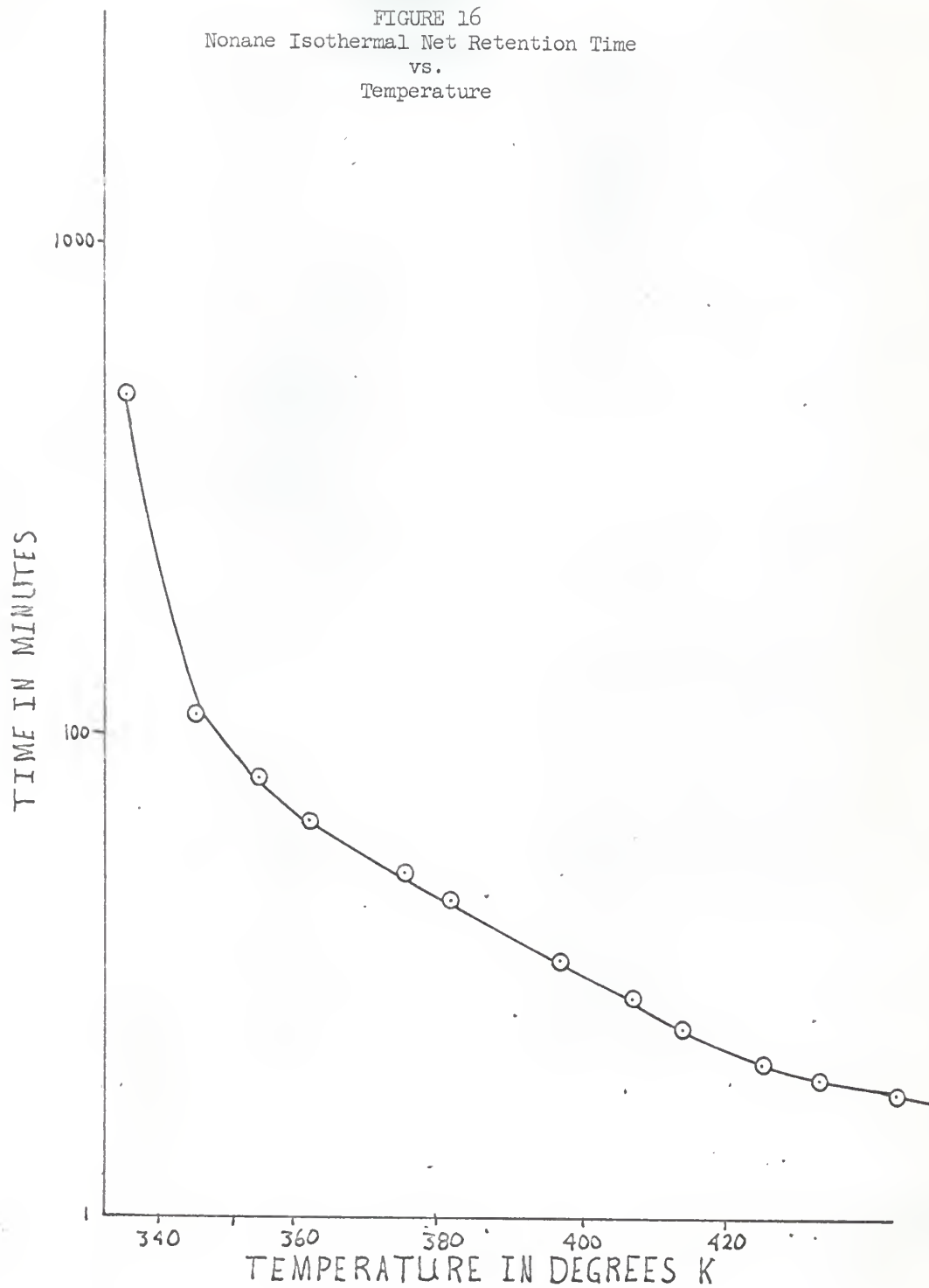


FIGURE 17

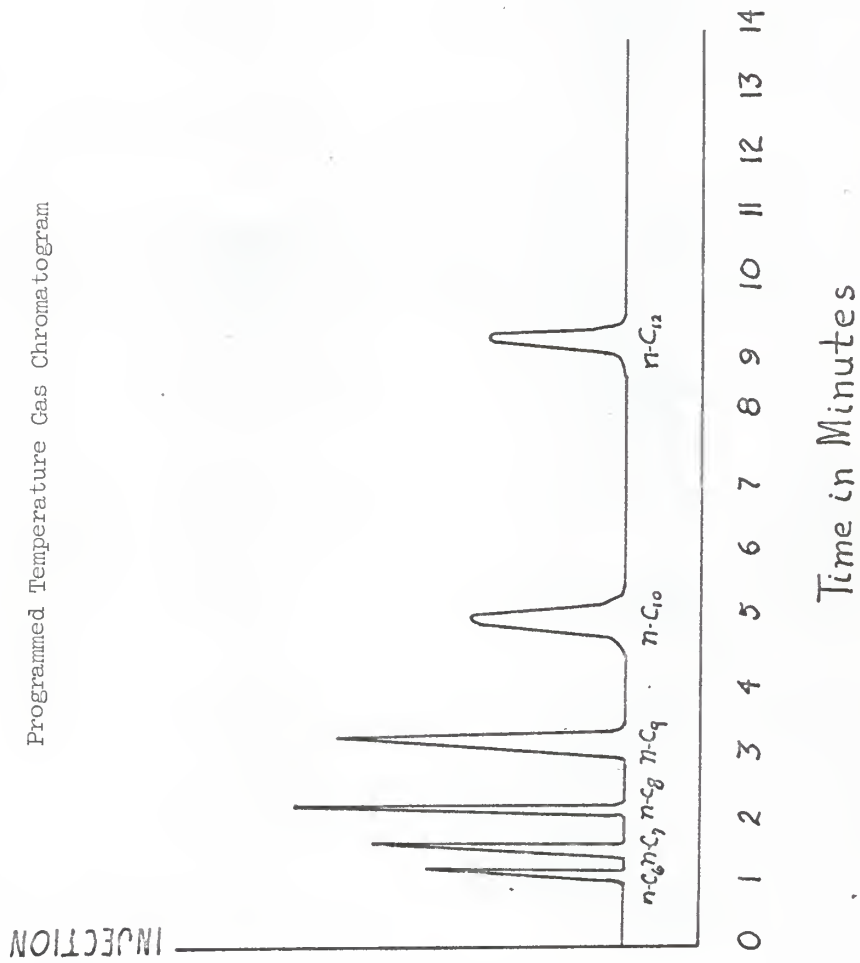
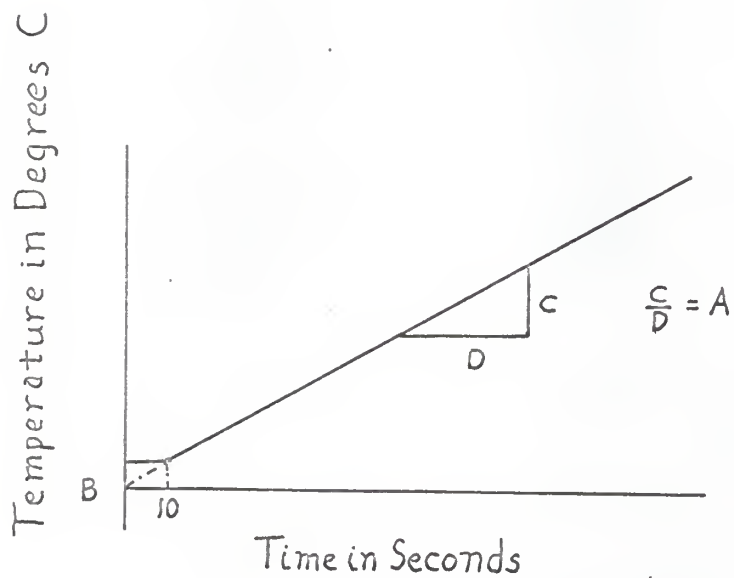




FIGURE 18

Heating Curve for Ideal Time-Temperature Program



column did not change instantly. The thermostat and column used could be operated so that there was a temperature lag or lead, neither of which is desirable for linear programs. The thermostat controls were set for a temperature lead and then altered so that the column would border on the conditions that would allow a temperature lag. Representative results are shown in Table 4. The column could be operated so that the time difference between actual start and calculated start was as short as 0.5 seconds or less.

Computation of programmed temperature retention times from isothermal data were based on the relationship

$$L = \int_0^{t'_R} u_s dt \quad (26)$$

in which  $u_s$  was the instantaneous sample velocity. Three factors entered into the calculation of  $u_s$ : position, average gas flow rate, and partition coefficient. The position factor was computed from equation (5), the other two factors were obtained from isothermal data. An I.B.M. 1640 computer was programmed to compute the progression of a sample component in a series of small time increments, until the total linear distance traveled exceeded column length. The total time required was determined from an average of time required for a component to reach the approximate end of the column and the next time period during which the component elutes from the column.

In order to solve equation (26) the right side of the equation must be a function of  $t$  only. The instantaneous sample velocity is a function of  $k$  and  $\bar{u}_x$  and position

TABLE 4

## Representative Results

Plateau time delay	Heating rate	Difference between actual delay and calculated delay	
sec.	$^{\circ}\text{C}/\text{min}$	sec.	$^{\circ}\text{C}$
10	4.90	-4.4*	-0.4
10	9.19	-2.5*	-0.4
10	13.78	-0.4	-0.1
10	5.02	0.0	0.0
20	12.76	0.5	0.1

\* The large delay was due to operator error.

$$u_s = \frac{f(x)\bar{u}}{1+k} \quad (27)$$

Therefore

$$u_s = f(x) \frac{L}{t_r \text{ isothermal}} \quad (28)$$

Thus equation (26) can be written

$$L = f(x) \frac{L}{t_r \text{ isothermal}} (\Delta t) \quad (29)$$

Where

$$t_r \text{ isothermal} = f(t) \quad (30)$$

Now

$$L = \sum_{i=0}^n f(x) \frac{L}{t_r \text{ isothermal}} (\Delta t_i) = \sum_{i=0}^n f(x) f(t) L \Delta t_i \quad (31)$$

Where  $n\Delta t = t_r$  and  $f(x)$  can be computed from constants  $p_i$  and  $p_o$ .

Equation (9) relates average retention time to velocity at the outlet for the moving phase. Because  $u_o/u$  can be substituted for  $p/p_o$ , equation (8) may be changed to

$$u_o = \bar{u} \left( \frac{2}{3} \right) \left[ \frac{(p_i/p_o)^3 - 1}{(p_i/p_o)^2 - 1} \right] \quad (32)$$

where  $u_o$  is velocity at the end of the column,  $\bar{u}$  is the average velocity,  $p_i$  and  $p_o$  are inlet and outlet pressures respectively. Equation (32) can be simplified because  $p_i/p_o$  always equals 1.77 and the column length is constant:

$$u_o = \frac{61.0}{t'_R / 1.4207} \quad (33)$$

where  $t'_R$  is net retention temperature for a compound at temperature  $T$ .

Thus it is convenient to define a  $t''_R$  as:

$$t''_R = t'_R / 1.4207. \quad (34)$$

Then  $t''_R$  is a function of net retention time and can be used to relate  $\bar{u}$  to the velocity of the peaks at the end of the column,  $u_0$ .

The equation used for prediction of the velocity of a peak at position  $x$  at time  $t'$  is:

$$u_x = \frac{u_0}{\sqrt{\frac{x}{L} [(P_i/P_0)^2 - 1] + (P_i/P_0)^2}}. \quad (35)$$

Equation 35 can be rewritten as:

$$u_x = \frac{61}{t''_R \sqrt{-0.03496x + 3.1329}}. \quad (36)$$

Equation (36) shows how  $t'_R$  can be related to  $u_x$ . This equation can be substituted into equation (26) and then equation (26) can be integrated. This problem was done on the IBM 1410 computer by an average step integration. The form of the computer program is:

$$L = \int_0^{t_R} f(u_x) dt \approx \sum_{i=0}^n \frac{61}{t''_{Ri} \sqrt{-0.03496x_i + 3.1329}} \Delta t. \quad (37)$$

Where  $t'_R = n\Delta t$ .

The computer equation was:

$$u_x = \frac{61}{t''_x \sqrt{-P(DI_x) + Q}} \quad (38)$$

where  $x$  is zero when the component was injected. The  $t''_x$  was a function of both the component and the temperature and was obtained from isothermal

data. The  $DI_x$ , which equals  $x$ , the position of the peak (see Fig. 19), was zero when  $x$  is zero and computable when  $x$  was greater than zero.

In equation (38)

$$P = \frac{1}{L} \left[ (P_i/P_o)^2 - 1 = 0.03496 \right] \quad (39)$$

and

$$Q = (P_i/P_o)^2 = 3.1329 . \quad (40)$$

When  $x$  was 11, the time elapsed was calculated by  $iR+10$  ( $R$  was inverse heating rate in seconds/ $^{\circ}C$ ).

The best velocity for a peak during an increment  $\Delta t_T$  is the average velocity of the gas obtained due to the change in position and temperature. This average was approximated by using the  $u_x$  to predict where the gas will be at  $(x+1) R+10$ , then by finding the velocity there by

$$u_{x+1} = \frac{61}{t_{x+1}'' \sqrt{-P(DI_{x+1}) + Q}} \quad (41)$$

where

$$\Delta t(u_x) = \Delta DI'_x \quad (42)$$

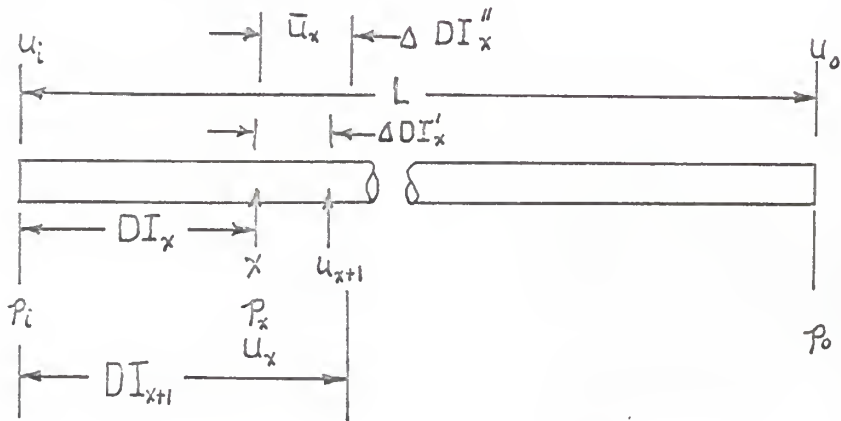
$$DI_{x+1} = DI_x + \Delta DI'_x . \quad (43)$$

The  $\Delta DI'_x$  was the predicted distance the peak would travel during the time increment. Then

$$\bar{u}_x = \frac{u_x + u_{x+1}}{2} . \quad (44)$$

The step integration was done by finding the distance traversed during time,  $\Delta t$ , by:

FIGURE 19

Diagram of Method for Calculation of  $t_R$ 

$$L = \int_0^{t_R} u_s dt \approx \sum_{i=0}^n f(u_x) \Delta t, \text{ stop when summation equals } L, \\ t_R = n \Delta t + t_0$$

$$\Delta DI'_x = \bar{u}_x \Delta t \quad (45)$$

where  $t$  is equal to  $R$ . The distance traveled during time  $xR+10$  was

$$DI_x = \sum_{i=1}^x \Delta DI'_{x_i}. \quad (46)$$

The net retention time for a compound at a given temperature represented one piece of information. The pieces of information were arranged into a progression so that the retention time, at  $1^\circ\text{C}$  increase, followed the previous one. This information was used in the computation and referred to as the "data pack".

The net retention times from programmed runs were compared with the calculated values (Table 5). The time required for the temperature to rise  $1^\circ\text{C}$  after the plateau was  $R$ . The rate of temperature rise,  $R$ , was the value used in calculating the net retention time. The deviation, abbreviated dev. in the table, was the difference between observed value and the calculated value.

The percent deviation would be expected to decrease as the retention times increase, if the heating rate had random errors. (The sum of the deviations would be zero.) However, the observed time deviation was nearly constant and always positive so the error was not pure random heating error.

If the system had a time lag, the largest percent error and smallest time deviation would be for the least retained component. The least retained component, hexane, which was mobile at starting conditions, had similar time deviations as the more retained components which were immobile at the starting conditions. Also the same time deviations were



TABLE 5

Comparison of Experimental Values With Calculated Values

Component	R sec/°C	t' <sub>R</sub>				Recalculated t' <sub>R</sub>	
		obs	cal	dev		dev	
		sec	sec	sec	%	sec	%
Hexane	12.0	12.7	9.5	3.2	34.8	0.4	4.2
Heptane	"	25.2	22.7	2.5	11.0	-0.3	-1.3
Octane	"	50.6	48.5	2.2	4.5	-0.6	-1.2
Nonane	"	92.7	89.6	3.1	3.4	0.3	0.3
Decane†	"	165.2	179.8	-14.6†	-8.1†	---	---
Dodecane	"	398.9	397.0	1.9	0.5	-1.1	-0.3
Hexane	7.02	14.6	11.3	3.3	29.2	0.5	4.4
Heptane	"	30.2	26.8	3.4	12.7	0.6	2.2
Octane	"	58.9	57.6	1.3	2.4	-1.5	-2.6
Nonane	"	106.4	102.5	3.9	3.8	1.1	1.1
Decane†	"	170.8	187.8	-17.0†	-1.1†	---	---
Dodecane	"	348.9	358.9	-10.0	-2.8	-12.8	-3.6
Hexane*	4.70	12.7	9.6	3.1	32.2	0.3	3.1
Heptane*	"	23.3	20.0	3.2	16.0	0.4	2.0
Octane*	"	43.9	40.1	3.8	9.5	1.0	2.5
Nonane*	"	77.1	70.2	6.9	9.8	4.1	5.9
Decane†*	"	123.9	133.5	-9.6†	-7.2†	---	---
Dodecane*	"	248.9	242.9	6.0	2.5	3.2	1.3

† Deviation for compound constantly low.

\* The heating rate is nonlinear.

observed for R1 and R2; this was not expected. The time lag depends on the heating rate; therefore, the time lag should vary with R. The error is constant for most compounds in R1 and R2; hence the error is probably not due to a lag.

Nonlinear heating would cause an increasing or a decreasing deviation as the time increased. Also the deviations would be all positive or all negative in all cases. This does not seem to be the case; besides, the deviations in R1 and R2 are not similar to the deviations in R3 which has a known nonlinear heating rate.

Another possibility is that the method of prediction has some error. The constant time deviation seems to indicate that some constant factor such as  $t_a$ , dead time, has been neglected. If the average deviation is calculated (excluding the one constantly low value) and if this average deviation in seconds is added to each of the calculated net retention times, the recalculated net retention time deviations can be found. If the errors in the method are random, both positive and negative deviations will occur. If the heating rate is linear, as the time temperature plot indicates, the percent errors should be about equal. The adjusted net retention deviation behaves the way one would expect and this indicates that the method of calculation has a constant and removable error. If the program is nonlinear, as is R3, the corrections will not help and the errors will not subtract out.

The average constant deviation in seconds is equal to twice the error introduced by the read-out system; therefore, the least one can say for the system is that it is as good or better than the present systems and possibly much better.

## SUMMARY AND CONCLUSIONS

A thermostat which has a predictable linear heating rate has been designed and developed. Solutions to problems such as measuring the column temperatures at a small time lag have been developed. The major problems in ohmic heating, nonlinear heating, and practical insulation of the column from other parts of the instrument have been solved for the system used. It was found that the prepacked stainless steel column used did not have any observable end effects. The instrument provided useful data for both isothermal and programmed temperature gas-liquid chromatography.

This thermostat, which was made from readily available materials, functions as well as (and possibly better than) the read-out system. The results of the experiments with the thermostat indicates that a thermostat for packed columns and capillary columns can be built which will have a predictable linear heating rate and a time lag of 3 seconds or less.

## SUGGESTIONS

The results of the experiments indicate improvements that could be made for a thermostat based on a guard system. The injection port should be mounted so that it is thermally insulated from the thermostat, and the temperature effects from the heat of the injection port and tubes connecting with the column should be minimized.

The injection port should hold a constant temperature; thus a more elaborate system for temperature than a variable transformer is desirable.

The time constant for the thermostat could be increased by closer control of the air bath temperature. The column container will have to be altered to achieve this.

Before the thermostat can be operated without excessive down time, the temperature sensors must be improved. The sensors used were available, inexpensive, and functionable, but they were the main factor causing down time. All other parts were satisfactorily reliable.

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TEMPERATURE PROGRAMMING IN GAS CHROMATOGRAPHY

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Stillwater, Oklahoma

1963

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## Abstract

A thermostat has been developed for use in programmed temperature gas chromatography. The design is based on direct ohmic heating of the column under conditions of minimum heat transfer from and to the surroundings. This is achieved by control of the thermostat air in such a way that the temperature difference between the column and the thermostat air is kept small at all times.

Constructions were developed to insulate the column electrically without introduction of excessive dead volume, and to minimize thermal end effects. Heat effects due to variations in electrical resistance of the column caused by work hardening were found to be negligible if suitable precautions were taken during forming and mounting of the stainless steel column. Response of the system was studied by means of 0.13 millimeter copper-constantan thermocouples mounted on the column by spotwelding, cementing, and soldering. Spot welded sensors were found to give the best results.

Gas chromatographic performance was studied by a comparison of retention data obtained during an actual programmed temperature run, which was predicted to be linear from the heat input, with data computed from a series of isothermal runs on the same column. The experimental data for a series of n-alkanes agreed to about 2% with data computed under the assumption of a linear time-temperature program.